

Triazolylstyryl compounds

Patent Number: US3891632

Publication
date: 1975-06-24

Inventor(s): FLECK FRITZ; SCHMID HANS RUDOLF

Applicant(s): SANDOZ LTD

Requested
Patent: GB1398993

Application
Number: US19730345677 19730328

Priority Number (s): US19730345677 19730328; CA19720150018 19720823; CH19690008647 19690606; CH19690008889 19690611; CH19710009025 19690606; CH19710009172 19690606; GB19720035631 19720731; US19700041055 19700527

IPC
Classification: C09B23/14

EC
Classification: C07D249/06; C07D249/20; C07D249/22; C07F9/6518G; D06L3/12; D06L3/12B6

Equivalents: BE751417, CA997339, CH523897, CH523900, CH523901, CH562812, DE2025792, FR2049917, GB1273478, NL7007631

Abstract

Triazolylstyryl compounds of formula WHEREIN R1 is hydrogen, lower alkyl or aryl, R2 is optionally substituted aryl, E1 is optionally substituted 4-(benzoxazolyl-2')-phenyl, 4-(naphthoxazolyl-2')-phenyl or (2'-phenyl-triazolyl-4')-styryl.

Data supplied from the esp@cenet database - I2

Description

The invention relates to triazolylstyryl compounds of formula ##SPC2##

Where A1 stand for one of the radicals ##SPC3##

R1 stands for hydrogen, alkyl with 1-6 carbon atoms, which may bear as substituents hydroxy, halogen or alkoxy with 1-6 carbon atoms, or phenyl, which may bear as substituents halogen, nitrile, alkyl or alkoxy with 1-6 carbon atoms, phenyl; the sulphonic or carboxylic group or the sulphonic or carboxylic amide group,

R2 stands for a phenyl or naphthyl radical, which may be substituted,

X1 stands for hydrogen, halogen, alkyl or alkoxy with 1-6 carbon atoms, or a phenyl, naphthyl, phenoxy or phenylalkyl radical which may be substituted and in which alkyl is of 1-6 carbon atoms,

X2 stands for hydrogen or alkyl with 1-6 carbon atoms,

X3 stand for hydrogen, halogen or alkyl or alkoxy with 1-6 carbon atoms

And the ring B may bear a substituent, provided that the substituents of the ring B and of phenyl radicals occurring in R2 and X1 are selected from the following: alkyl or alkoxy with 1-6 carbon atoms, halogen, nitrile, unsubstituted or substituted phenyl or phenoxy, carboxylic or sulphonic acid, carboxylic or sulphonic acid phenyl, substituted phenyl or optionally substituted alkyl (C1-6) ester, carboxylic or sulphonic acid amide, optionally substituted phenylsulphonyl, alkylsulphonyl with 1-6 carbon atoms, where alkyl may bear as substituents hydroxy, halogen or alkoxy with 1-6 carbon atoms and phenyl and phenoxy may bear as substituents alkyl (C1-6), alkoxy (C1-6) or halogen; and that the amides derive from amines of formula ##SPC4##

PATENT SPECIFICATION

(11) 1 398 993

1 398 993

- (21) Application No. 35631/72 (22) Filed 31 July 1972
 (61) Patent of Addition to No. 1 273 478 dated 5 June 1970
 (44) Complete Specification published 25 June 1975
 (51) INT CL³ C07D 249/06
 (52) Index at acceptance
 C2C 1450 200 215 220 226 22Y 246 250 252 25Y 28X 30Y
 313 31Y 338 342 34Y 366 367 396 43X 551 574
 579 613 61X 628 62X 668 699 775 77X 77Y 794
 797 BK KF QN ZD

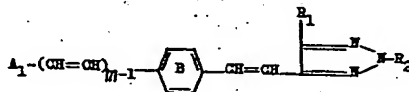
72 Inventors FRITZ FLECK and HANS-RUOLF SCHMID



(54) IMPROVEMENTS IN OR RELATING TO TRIAZOLYLSTYRYL COMPOUNDS

(71) We, SANDOZ LTD., of 4002 Basle, Switzerland, Lichtstrasse 35, a Body Corporate organized according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to triazolylstyryl compounds, a process for their production and their use for brightening organic materials; it is an improvement in or modification of the invention described and claimed in Patent No. 1,273,478, i.e. a triazolylstyryl compound of the formula



where

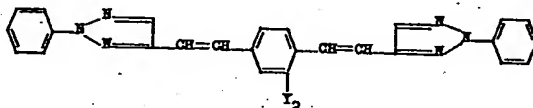
R₁ represents a hydrogen atom, an alkyl radical with 1 to 6 carbon atoms which may be substituted or a mononuclear or binuclear aryl radical which may be substituted,

R₂ represents a mononuclear or binuclear aryl radical which may be substituted,

A₁ represents a five-membered heterocycle with 2 or 3 nitrogen atoms or 1 oxygen atom and 1 nitrogen atom which heterocycle may be substituted, and

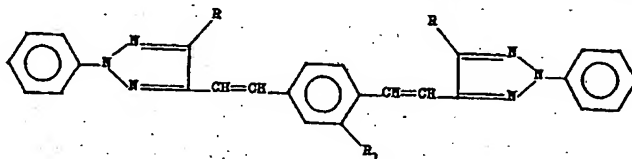
m is 1 or 2,

with the proviso that the benzene nucleus B may be substituted, providing that when A₁ represents a benzo, naphtho- or acenaphtho-triazole radical and m is 1 any substituent on nucleus B must be selected from arylsulphonyl radicals and first order substituents as defined in said patent; preferred triazolylstyryl compounds described and claimed in said patent are those of the formula



where Y₂ represents a hydrogen or chlorine atom, a cyano or alkyl radical with 1 to 6 carbon atoms, an alkoxy-carbonyl or aminocarbonyl radical which may be substituted, an alkylsulphonyl radical with 1 to 6 carbon atoms, a sulphonic acid radical, or a sulphonic acid alkyl ester, sulphonic acid arylester or sulphonic acid amide radical which may be substituted.

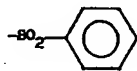
The present invention provides a triazolylstyryl compound of the formula



[Price 33p]

in which

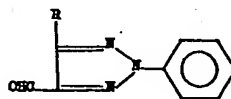
R represents hydrogen or methyl, and
 R_1 represents $-\text{CONH}_2$, $-\text{COOH}$, $-\text{SO}_2$



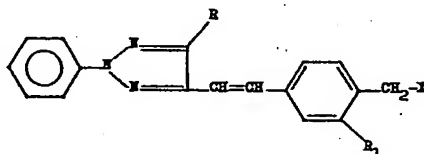
5 halogen or hydrogen,
 with the proviso that both R and R_1 cannot represent hydrogen simultaneously. 5
 When the radical R_1 is halogen, it is preferred that this should be chlorine or bromine.

10 The compounds of the present invention may be synthesized by any one of the various methods known for analogous reactions, especially the ones described and claimed in said prior patent. 10

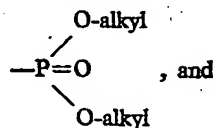
The preferred route of synthesis according to the present invention is characterised in that a triazolylaldehyde of the formula



15 where R has the above meaning,
 or a functional derivative thereof, e.g. an oxime, hydrazone or anil, is condensed with a substituted toluene of the formula 15



where X represents H, $-\text{CN}$, $-\text{COOH}$ or




20 , and 20

R and R_1 have the above meanings,
 in the presence of a condensation catalyst such as boric acid, zinc chloride, an arylsulphonic acid, e.g. benzene- or 4-methylbenzene-sulphonic acid, acetic anhydride, an alkali metal acetate, e.g. sodium or potassium acetate, piperidine, an alkali metal salt or alkaline earth metal salt of an arylsulphonamide, e.g. the sodium, potassium, calcium or barium salt of benzene- or 4-methylbenzene-sulphonamide, and an hydroxide or alcoholate of an alkali metal or alkaline earth metal, e.g. the sodium, potassium, calcium or barium hydroxide or alcoholate, preferably in the absence of air at temperatures ranging from 0° to 200°C or more, especially at 20° to 160°C . When X is hydrogen, the progress of the reaction is facilitated when the benzene nucleus bears a second order substituent (i.e. meta-directing), e.g. $-\text{COOH}$ or $-\text{CONH}_2$. On completion of the reaction the group X, if still present, is split off by in conventional manner.

25 The reaction can be carried out in the melt or in an inert solvent e.g. an aliphatic or aromatic, preferably halogenated, hydrocarbon, alcohol, ether, glycol, or formamide, dimethyl formamide, dimethyl acetamide, N-methylpyrrolidone, acetonitrile, dimethyl sulphoxide, tetramethylene sulphone or phosphoric acid tris-(dimethylamide). 25

30 The compounds of the present invention generally have properties similar to the properties mentioned for the triazolyl compounds of said prior patent and may be employed in like manner to that described therein. 30

40 The following Examples illustrate the present invention without limiting it. 40

Ex. No.	R	R ₁	m. p.	λ _{max}
1	H	-CONH ₂	300-302°C	368 [in (CH ₃) ₂ SO]
2	H	-COOH	272-279°C	
3	H	Cl	223-224°C	365 [in (CH ₃) ₂ SO]
4	H	-SO ₂ - 	225-227°C	370 [in (CH ₃) ₂ SO]
5	CH ₃	H	203-204°C	373 [in CHCl ₃]

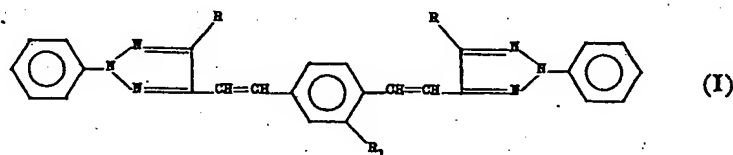
The procedure used in producing the above five compounds is that specifically described in any one of examples 1 to 3 of said prior patent, the starting materials being chosen in each case so as to give rise to the required end product.

5

WHAT WE CLAIM IS:—

1. A triazolylstyryl compound of the formula (I),

5

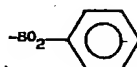


in which

R represents hydrogen or methyl, and
R₁ represents -CONH₂, -COOH,

10

10



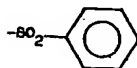
halogen or hydrogen,

with the proviso that both R and R₁ cannot represent hydrogen simultaneously.

15

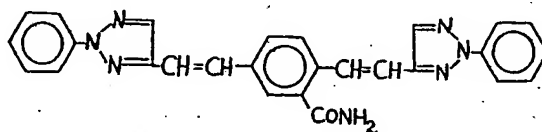
2. A triazolylstyryl compound according to Claim 1, and of the formula I, in which R represents hydrogen and R₁ represents -COOH or

15

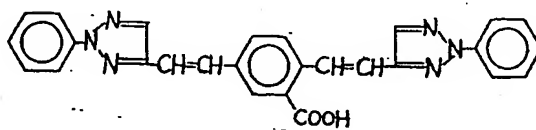


3. A triazolylstyryl compound according to Claim 1, in which R represents methyl.

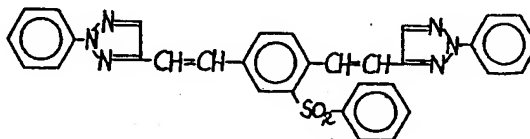
4. The compound of formula



5. The compound of formula



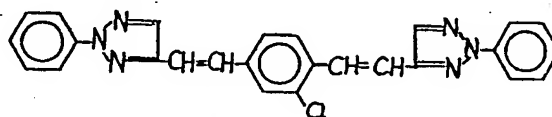
6. The compound of formula



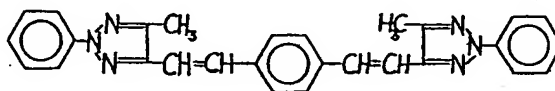
5

7. The compound of formula

5



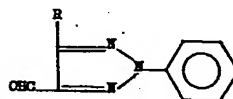
8. The compound of formula



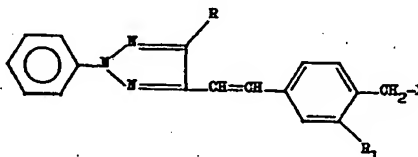
10

9. A process for the production of a triazolylstyryl compound according to Claim 1, characterised in that a triazolylaldehyde of the formula

10



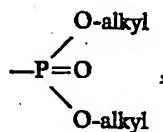
in which R is as defined in Claim 1, or a functional derivative thereof, is condensed with a substituted toluene of the formula



15

where X represents H, —CN, —COOH or

15



and R₁ is as defined in Claim 1, in the presence of a condensation catalyst.

10. A process according to Claim 9, substantially as herein described.
11. A compound according to Claim 1, whenever produced by the process claimed in Claim 9 or Claim 10.
12. A method of brightening an organic material comprising applying thereto a compound as claimed in any of Claims 1 to 8 and 11.
13. A method according to Claim 12, substantially as herein described.
14. An organic material whenever brightened by a compound as claimed in any one of Claims 1 to 8 or 11.

B. A. YORKE & CO.,
Chartered Patent Agents,
98, The Centre,
Feltham,
Middlesex TW13 4EP.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.